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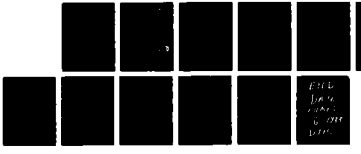

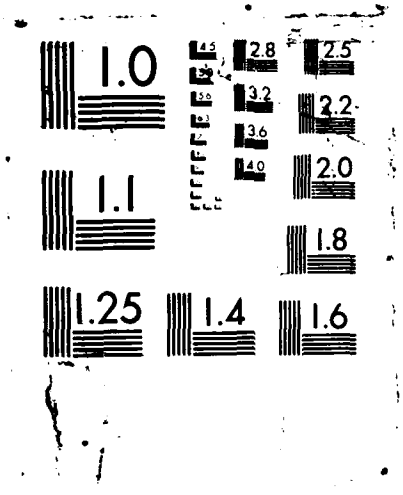
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by

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This paper summarizes some past and recent work from the author's laboratory on the reactions of carbon dioxide with metal complexes with the objective of suggesting the relevance of this research to some related biological systems. First, the various CO_2-metal complex interactions *in vivo* and *in vitro* are briefly cited, followed by a description of the reversible activation of carbon dioxide by model rhodium and iridium compounds. Finally, recent results are presented on homogeneous catalytic hydrogenation/reduction of CO_2 mediated by metal complexes, including a platinum cluster complex which catalyzes the carbon dioxide conversion at mild conditions

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CATALYTIC ACTIVATION OF CARBON DIOXIDE BY METAL COMPLEXES

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Summary

This paper summarizes some past and recent work from the author's laboratory on the reactions of carbon dioxide with metal complexes with the objective of suggesting the relevance of this research to some related biological systems. First, the various CO_2-metal complex interactions *in vivo* and *in vitro* are briefly cited, followed by a description of the reversible activation of carbon dioxide by model rhodium and iridium compounds. Finally, recent results are presented on homogeneous catalytic hydrogenation/reduction of CO_2 mediated by metal complexes, including a platinum cluster complex which catalyzes the carbon dioxide conversion at mild conditions.

CO_2-metal complex interactions in nature [1,2]

It has been said that "two chemical individuals stand alone in importance for the great biological cycle upon the earth. The one is water, the other carbon dioxide ... " [3]. Many of these vital CO_2 reactions in living systems involve metal complexes [2]. For example, (i) zinc is an essential ingredient for the activity of the enzyme (En) carbonic anhydrase, which catalyzes the hydration-dehydration of carbon dioxide. The first step in the suggested mechanism of the CO_2 conversion is the formation of a bicarbonato complex (eqn. 1) [4]. (ii) There are numerous

$$\text{En-Zn-OH} + CO_2 \rightleftharpoons \text{En-Zn-OC(O)OH} \qquad (1)$$

and complex metabolic carboxylation reactions catalyzed or assisted by enzymes containing metal ions or requiring them as cofactors (abbreviated and schematically depicted in eqns. 2a,b,c) [5]. (iii) The carbon dioxide

$$\text{R-C(H)(H)} + CO_2 \xrightarrow[\text{Enzyme}]{Mg^{2+} \text{ or } Mn^{2+}} \text{R-C(H)(C(O)OH)} \qquad (2a)$$

$$\text{R-N(H)-H} + CO_2 \xrightarrow[\text{Enzyme}]{Mg^{2+}} \text{R-N(H)-C(O)OH} \qquad (2b)$$

$$\text{Ferredoxin}(Fe^{2+}) + CO_2 + H^+ \longrightarrow HC(O)OH + \text{Ferredoxin}(Fe^{3+}) \qquad (2c)$$

fixation in photosynthesis (eqn. 3) [6] includes a series of photochemical,

$$6CO_2 + 6H_2O \xrightarrow[\text{Chlorophyll, enzymes}]{h\nu\ (Mg^{2+},\ Mn^{2+},\ Fe^{2+/3+})} C_6H_{12}O_6 + 6O_2 \qquad (3)$$

redox and enzymatic reactions with the participation of various biochemical metal complexes, although these species appear to have only an indirect role in the conversion of CO_2 to carbohydrates. (iv) The reactions of carbon dioxide with amino groups in the protein part of hemoglobin (Hb) to form carbamates (eqn. 4) in the respiratory process [7] might also be

$$Hb\text{-}NH_2 + CO_2 \rightleftharpoons Hb\text{-}NH\text{-}C(O)OH \qquad (4)$$

mentioned. These interactions do not directly involve a metal center (Fe in Hb), but they are related to some CO_2 fixations catalyzed by synthetic metal complexes (see eqn. 16 below).

Model compounds: CO_2 in synthetic coordination chemistry [8-12]

The last two to three decades have seen an emergence and development of a versatile and extensive field of chemistry which embraces the fundamental study and practical applications of the activation of small molecules by synthetic metal complexes (eqn. 5) [13-15]. This general field of

$$ML_i + XY \rightleftharpoons (XY)ML_i \qquad (5)$$

M = metal atom; L_i = ligands; XY = H_2, O_2, N_2, C_2H_4, CO, CO_2, etc.

study has had an important impact on other areas of science as well, notably organometallic chemistry [14,15], homogeneous catalysis [14-17], and bioinorganic chemistry [18]. As the latter term implies, our percep-

tions of certain biochemical reactions can also profit from the knowledge of analogous inorganic systems. The objective is to find simple synthetic models for complex biological processes, and thus possibly gain insights into the functions of metalloenzymes and other metal-containing species *in vivo*.

The activation of carbon dioxide by metal complexes is of relatively recent origin, but the field has developed into a substantial area of coordination chemistry. There are two general types of CO_2-metal complex interactions: (i) a direct attachment of carbon dioxide to the metal atom in a complex, *M* (eqn. 6), and (ii) insertion of CO_2 into a metal-ligand

$$M + CO_2 \longrightarrow M\text{-}CO_2,\ M\text{-}OCO \qquad (6)$$

bond (eqn. 7). In each category, different modes of carbon dioxide

$$M\text{-}L + CO_2 \longrightarrow M\text{-}OC(O)L \qquad (7)$$

$L = H,\ OH,\ NR_2,\ CR_3$, etc.

coordination have been established or recognized. Some simplified examples are depicted in eqns. (6) and (7) (which exclude details of bonding and more complicated types of CO_2 compounds) [8-12]. In all these metal complex-CO_2 interactions, the symmetry and the carbon-oxygen bond order (B.O. = 2) of free carbon dioxide are lowered in the process, i.e., the CO_2 becomes "activated". Thus, these reactions (eqns. 6, 7) are being considered as critical first steps in the development of catalytic reductions of carbon dioxide.

Relatively few actual catalytic reactions of CO_2 promoted by transi-

tion metal complexes have been reported [11,12,19-21]. They include the hydrogenation/reduction of carbon dioxide in the presence of amines or alcohols and lead to formamide/formate types of products (eqn. 8). These

$$CO_2 + H_2 + R_2NH,\ ROH \xrightarrow{\text{Metal complex}} HC(O)NR_2,\ HC(O)OR + H_2O \qquad (8)$$

catalyses have been carried out mostly at elevated pressures and temperatures in alcohol or benzene solutions and mediated by a variety of organometallic complexes. Some mechanistic studies of reactions (8) have also been reported [19,20c,21].

It should be noted that besides finding models for carbon dioxide reactions in nature, the research on the activation of CO_2 by metal complexes has another important objective. Carbon dioxide is an abundant and inexpensive potential source of carbon for synthetic chemicals, including fuels, and its catalytic reduction is therefore of great scientific as well as economical interest.

Reversible activation of CO_2 by rhodiun and iridium complexes [22-25]

Our interest in the catalytic activation of carbon dioxide originates from the discovery that certain hydroxo complexes of iridium and rhodium, $[M(OH)(CO)(Ph_3P)_2]$ (M = Ir, Rh) [26], react *reversibly* with CO_2 at ambient conditions (eqn. 9). The reactions take place between the crystalline

$$[(Ph_3P)_2(CO)M(OH)] + CO_2 \rightleftharpoons [(Ph_3P)_2(CO)M(OC(O)OH)] \qquad (9)$$

complexes and gaseous carbon dioxide, and were first interpreted as CO_2-metal complex adducts [23]. Subsequent work by others suggested that

they actually contain coordinated bicarbonate M-OC(O)OH (eqn. 9, cf. eqn. 1) [27]. On dissolution in ethanol, the complexes apparently react with the solvent alcohol to yield ethylcarbonato compounds (eqn. 10) [27a]

$$[(Ph_3P)_2(CO)M(OC(O)OH)] + C_2H_5OH \rightleftharpoons [(Ph_3P)_2(CO)M(OC(O)OC_2H_5)] + H_2O \quad (10)$$

(these were formulated as bicarbonato complexes in our original communication [22]). The products of reactions (9) or (10) with M = Rh undergo acid-base type substitution reactions with a variety of species (eqn. 11);

$$Rh\text{-}X + Y \longrightarrow Rh\text{-}Y + X \quad (11)$$

$Rh = (Ph_3P)_2(CO)Rh$; $X = OC(O)OH^-$ or $OC(O)OC_2H_5^-$

$Y = Cl^-, SH^-, H_2PO_4^-, SO_4^{2-}, OC_2H_5^-$

with M = Ir, oxidative addition reactions with hydrogen and oxygen are observed. The hydroxo complexes react also with carbon oxysulfide, COS, giving analogous products (eqn. 9) which, collectively, testify to the varied and extensive chemistry of carbon dioxide activation by these synthetic metal complexes [22-24].

The factors influencing the reactivity of carbon dioxide toward transition metal complexes and the stability of the resulting CO_2-metal associations appear to be, in general, related to metal basicity (or acidity) which has been found to determine the activation of other "acidic" (O_2, H_2, etc.) or "basic" (C_2H_4, CO, etc.) molecules (eqn. 5) [13,28]. In our model compounds, $[M(A)(CO)L_2]$ (M = Ir, Rh; A = univalent anionic ligand, OH^-, Cl^-, etc. [26]; L = neutral ligand, e.g., Ph_3P), there is a unique spectroscopic label, the vibrational frequency of the coordinated

carbon *monoxide*, ν_{CO}, which reflects the relative basicity of the metal center in these complexes [26]. The ν_{CO} also sensitively responds to addition reactions of $[M(A)(CO)L_2]$ with a variety of molecules, XY, producing $[(XY)M(A)(CO)L_2]$ (cf. eqn. 5). The direction and magnitude of $\Delta\nu_{CO}$ accompanying these reactions allows one to assess the acidity or basicity - and the reactivity - of XY relative to the particular derivatives of $[M(A)(CO)L_2]$, and predict the stability of the adducts [13,28].

The formation of the bicarbonato complexes (eqn. 9) represents an insertion of CO_2 into the M(OH) bond (M-OH or MO-H). The corresponding chloro complexes, $[M(Cl)(CO)(Ph_3P)_2]$ (and other non-hydroxo species, A = F, Br, I, etc.), on the other hand, do not measurably react either as solids or solutions with CO_2 under *one atm* (25°C), apparently because they lack an appropriate ligand for insertion. Recent experiments under elevated carbon dioxide pressures, however, show that these complexes do react with CO_2 under these conditions forming addition compounds (eqn. 12,

$$[M(Cl)(CO)(Ph_3P)_2] + CO_2 \underset{CHCl_3}{\overset{7\text{-}65\ atm}{\rightleftharpoons}} [(CO_2)M(Cl)(CO)(Ph_3P)_2] \qquad (12)$$

M = Ir, Rh) [25]. On exposure to carbon dioxide, the original ν_{CO} absorption bands in the spectra of $[M(Cl)(CO)(Ph_3P)_2]$ at 1975 (Rh) and 1965 cm^{-1} (Ir) gradually shift to 1959 and 1949 cm^{-1}, respectively, indicating complete conversions to the CO_2 complexes (eqn. 12). Depressurization leads to the reappearance of the starting materials. Due to the low solubilities of the CO_2 complexes, the IR absorption bands derived from the coordinated carbon dioxide have not yet been located, and the type of metal-CO_2 bonding (see eqn. 6) is thus unknown at present. The important observation, however, is that the CO_2 addition reactions (eqn. 12) are

accompanied by a ν_{CO} shift to *lower* frequencies, albeit by a small amount, $\Delta\nu_{CO}$ = 16 cm^{-1} for both reactions, M = Rh, Ir. According to our previous interpretation [13,28], the direction and extent of this ν_{CO} shift implies that carbon dioxide acts as a *weak base* toward these particular complexes, $[M(Cl)(CO)(Ph_3P)_2]$. The IR data are also consistent with the ready reversibility of the carboxylations (eqn. 12). By using FT-IR techniques *in situ*, these studies are being extended to include other metal complexes with the objective of quantitatively assessing the electronic and stereochemical nature of CO_2 activation.

Homogeneous catalysis of CO_2 hydrogenation/reduction [29,30]

Following the observations on the reversible CO_2 activation by $[M(OH)(CO)(Ph_3P)_2]$ (eqn. 9), our efforts were directed toward developing catalytic systems for the reduction of carbon dioxide based on these and other metal complexes, including clusters and metallic dispersions. One of our goals was to explore methods for reducing the carbon atom in CO_2 to a lower formal oxidation state than found in formamides and formates (2+) (eqn. 8) via homogeneous catalysis by metal complexes.

By employing several ruthenium, osmium, rhodium, iridium and platinum compounds as catalyst precursors for the previously reported carbon dioxide hydrogenation/reduction (eqn. 13) [19], we found that in addition to

$$CO_2 + H_2 + (CH_3)_2NH \xrightarrow[\text{Toluene}]{\text{Metal complex}} HC(O)N(CH_3)_2 + H_2O \qquad (13)$$

N,N-dimethylformamide (DMF), these solution catalyses yielded also trimethylamine (TMA) as a minor product with these selectivities: DMF,

85-99.5; TMA, 0.5-15 mol %. The reactions were carried out at 125°C and under total pressures of 96-133 atm (125°C) of the three reactant gases (eqn. 13). The turnover numbers (DMF or TMA (mol)/metal complex (mol)/day (24 hr reaction period)) ranged from 14-1460 for DMF and 0.4-52 for TMA, for different complexes [29].

The formation of trimethylamine by reaction (13) does not appear to have been reported previously, and it seemed that TMA is likely to result from the catalytic hydrogenation of DMF produced initially (eqn. 13). Accordingly, experiments were carried out by using neat DMF and hydrogen as starting materials, eqn. (14) (p_{H_2}, 102-115 atm at 150°C), in the presence

$$HC(O)N(CH_3)_2 + 2H_2 \xrightarrow{\text{Metal complex}} (CH_3)_3N + H_2O \qquad (14)$$

of the same metal complexes as employed in reaction (13). Several complexes were indeed found to be active in catalyzing the hydrogenation of DMF to trimethylamine (eqn. 14). These results, eqns. (13) + (14), thus point to the overall reduction of carbon dioxide to the methyl group ($-CH_3$, C^{2-}) incorporated in trimethylamine (eqn. 15). Both of the

$$CO_2 + 3H_2 + (CH_3)_2NH \xrightarrow{\text{Metal complex}} (CH_3)_3N + 2H_2O \qquad (15)$$

individual reactions, the DMF synthesis (eqn. 13) and its hydrogenation (eqn. 14), appear to be complex catalytic systems. For example, reaction (13) is always accompanied by a non-catalytic spontaneous formation of dimethylcarbamate (eqn. 16, cf. eqn. 4), a reversible reaction whose role

$$CO_2 + 2(CH_3)_2NH \rightleftharpoons [(CH_3)_2NH_2]^+[(CH_3)_2NC(O)O]^- \quad (16)$$

is under investigation, together with other elementary steps in these catalyses.

Another significant observation on the catalytic reduction of carbon dioxide was made during the course of investigating the DMF synthesis cited above (eqn. 13). A platinum cluster complex, $[Pt_2(\mu\text{-dppm})_3]$ (dppm = $Ph_2PCH_2PPh_2$) [31], was found to be an effective catalyst precursor for reaction (13) at unprecedentedly mild conditions [30]. The catalysis takes place at 25°C and is clearly observable even under a total pressure of less than one atm of the three reactant gases (eqn. 13). Furthermore, the reaction is readily *reversible*, an unusual observation in homogeneous catalysis by metal complexes. The reversibility of reaction (13) is evidenced by noting that the yield of DMF, obtained at initial stages of the reaction, diminishes by reducing the pressure, increasing the temperature, or both within the same experiments, in accordance with the thermodynamics of this process [30]. For example, at 100°C, the initial yield of 1375 TN (turnover number, see above) decreased to 996 TN by lowering the pressure from 114 to 1 atm; or at 0.9 atm, the yield decreased from 8.7 TN to 3 TN by increasing the temperature from 25° to 50°C [30].

The molecular structure of $[Pt_2(\mu\text{-dppm})_3]$ shows that the complex has two terminal vacant sites and a third one for the insertion into the Pt-Pt bond [31c]. These structural features are probably responsible for the facile catalysis with an apparently low activation energy. The complex appears to be ideally suited for the study of the mechanisms of the catalytic reduction of carbon dioxide (eqns. 13, 14), now in progress.

Concluding remarks

The purpose of this brief exposition was to report to researchers in enzyme science some inorganic chemical developments in carbon dioxide activation, and to suggest that the knowledge of these reactions may have something to contribute to the understanding of corresponding biochemical processes. Most of the biochemical carbon dioxide reactions mentioned at the outset have an analogy, however remote, in the inorganic realm: (i) CO_2 hydration-dehydration, eqns. (1) and (9); (ii) catalytic carboxylations, eqn. (2) and similar synthetic reactions presently under study in our laboratory; (iii) catalytic reductions, eqns. (3) and (8), (13), (14); and (iv) reversible carbamate formation, eqns. (4) and (16). The metal ions or central atoms in synthetic complexes have, of course, only primitive catalytic activity compared to their enzymatic counterparts, but the former are subject to much easier investigations due to the relative simplicity of the reacting systems and the availability of various physicochemical tools for the study of structure-function relationships and electronic mechanisms (cf. ν_{CO} in eqn. 12).

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